

A predictive systematization for ns^2 – nsn' p line strength data

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Abstract. A semiempirical formulation previously used to parametrize line strength data for ns^2 – nsn' p alkaline-earth-like resonance and intercombination transitions is extended to study the $2s^2$ – $2s3p$ and $3s^2$ – $3s4p$ transitions in the Be and Mg isoelectronic sequences. The approach utilizes measured lifetime and energy level data in a linearizing isoelectronic data mapping based on the empirical characterization of singlet–triplet mixing. Although this extension to extrashell transitions introduces complications from plunging configuration interaction, transition integral cancellations and multiple exit channels, the predictive regularities of this method are shown to persist, and to provide insights into the dynamical behaviour of these systems.

1. Introduction

In studies of ns^2 – nsn' p transitions in alkaline-earth-like isoelectronic sequences it has been shown (Curtis 1991) that measured decay lifetimes for the 1S_0 – 1P_1 resonance transition and for the 1S_0 – 3P_1 intercombination transition can be jointly represented as a spin-reduced empirical line strength, formulated through the use of a singlet–triplet mixing angle that is deduced from measured spectroscopic energy level data. It was also shown (Curtis 1991) that the dependence on nuclear charge Z of this reduced line strength can be presented in a linearizing semiempirical exposition that permits quantitative interpolation and extrapolation.

The purpose here is to demonstrate that this approach can be extended to study ns^2 – nsn' p transitions for $n' > n$, where the dynamics is complicated by the effects of configuration interaction, level crossings, transition integral cancellation and multiple exit channels. The $2s3p$ and $3s4p$ configurations in the Be and Mg isoelectronic sequences provide suitable examples for this study, because a novel experimental technique has been developed and applied to them (Engström *et al* 1978, Hardis *et al* 1983, Reistad *et al* 1984) which permits the determination of intercombination transition probabilities through differential decay curve measurements. Using empirical data reductions it is demonstrated below that, although transition probabilities, transition wavelengths and singlet–triplet mixing angles can exhibit strong local perturbations in their isoelectronic behaviour due to level crossings and other perturbations, the effective spin-reduced line strengths are regular, and can be predicted by linear parametrizations.

2. Intercombination rates from differential decay curve measurements

Lifetimes of the $2s3p$ 3P_J levels in the Be isoelectronic sequence have been the subject of a number of experimental (Engström *et al* 1979, Hardis *et al* 1983) and theoretical

(Hibbert 1979, Ellis 1983, Kim *et al* 1988) studies motivated by a measurement technique that exploits the J dependence of their exit channels. All three levels have similar electric dipole (E1) allowed decay branches to triplet levels in the $2p^2$ and $2s3s$ configurations, but the $J=1$ level has additional E1 intercombination branches to singlet levels in the $2s^2$, $2p^2$ and $2s3s$ configurations opened by spin-orbit induced singlet-triplet mixing, which increases with increasing Z along the sequence. If the J dependence of the triplet-triplet transition probabilities and the contributions of higher multipole moments can be neglected, then the algebraic difference between the reciprocal lifetime of the $J=1$ level and that of the $J=2$ or 0 level yields the sum of the transition probabilities of the intercombination branches. If branching to the ground $2s^2$ level dominates over that to the $2p^2$ and $2s3s$ levels then this differential lifetime measurement determines the $2s^2\ ^1S_0$ - $2s3p\ ^3P_1$ transition probability.

A homologous example exists for the $3s4p\ ^3P_J$ levels in the Mg sequence that also has been studied both experimentally (Reistad *et al* 1984) and theoretically (Reistad *et al* 1984, Godefroid and Froese Fischer 1985, Brage and Hibbert 1989). In this case the $3p3d$ configuration complicates the situation by introducing plunging configuration interaction and additional intercombination channels. The difference between the reciprocal lifetime of the $J=1$ level and that of the $J=2$ or 0 level yields here a transition rate that is primarily attributable to intercombination transitions from the $3s3p\ ^3P_1$ to singlet levels in the $3s^2$, $3s3d$, $3p^2$ and $3s4s$ configurations. However, the theoretical studies cited above have shown that for this case the sum of the singlet-triplet transition probabilities is not dominated by the branch to the $3s^2$ ground state, and that the triplet-triplet transition probabilities exhibit non-negligible J dependence in the vicinity of the $3p3d$ - $3s3p$ level crossing. As a result, the differential lifetime measurements available for S v and Cl vi do not yield a direct measure of the $3s^2\ ^1S_0$ - $3s4p\ ^3P_1$ transition probability, but a sum with other contributions. Nevertheless, the singlet-triplet mixing angle formulation does provide an empirical means for studying this system.

3. Computational formulation

The semiempirical data reduction method employed here consists of: (i) the specification of an effective single configuration singlet-triplet mixing angle ϑ from experimental energy level data; (ii) the use of ϑ and experimental wavelength data to construct a total effective $J=1$ line strength $S(\text{Tot})$ from experimental transition probability data. This procedure is described briefly below.

For a pure $nsn'p$ configuration, the singlet and triplet $J=1$ states can be written in terms of amplitudes expressible by a single mixing angle ϑ as

$$|^3P'_1\rangle = \cos \vartheta |^3P_1\rangle - \sin \vartheta |^1P_1\rangle \quad (1)$$

$$|^1P'_1\rangle = \sin \vartheta |^3P_1\rangle + \cos \vartheta |^1P_1\rangle \quad (2)$$

where the primes indicate the mixed states for which the LS labels are only nominal. If the excitation energies of the 3P_0 , $^3P'_1$, 3P_2 and $^1P'_1$ levels are denoted by E_{30} , E_{31} , E_{32} and E_{11} , it has been shown (Curtis 1989) that the mixing angle can be deduced from the measured spectroscopic data using

$$\cot(2\vartheta) = \pm \frac{1}{\sqrt{2}} \left(\frac{3(E_{31} + E_{11} - 2E_{30})}{2(E_{32} - E_{30})} - 1 \right). \quad (3)$$

The empirical eigenstates can be constructed from spectroscopic data using equations (1)–(3), and used to relate the radial dipole transition integrals to the line strengths for the ns^2 - $nsn'p$ resonance and intercombination transitions $S(\text{Res})$ and $S(\text{Int})$, which are given by

$$S(\text{Res}) = 2 \cos^2 \vartheta |\langle ns0|r|n'p0 \rangle|^2 \quad (4)$$

$$S(\text{Int}) = 2 \sin^2 \vartheta |\langle ns0|r|n'p1 \rangle|^2. \quad (5)$$

Here the ket vectors $|nIS\rangle$ denote the corresponding radial wavefunctions. Measured transition probabilities A for $J = 1$ level can be converted to line strengths by the relationship

$$S = 3[\lambda(\text{\AA})/1265.38]^3 A(\text{ns}^{-1}) \quad (6)$$

where λ is the transition wavelength. If the singlet-triplet splitting is small and the transition integrals do not have strong cancellation effects (Curtis and Ellis 1978) then $\langle ns0|r|np0 \rangle \approx \langle ns0|r|np1 \rangle$ and the total effective $J = 1$ line strength $S(\text{Tot})$ for the ns^2 - $nsn'p$ transition is given by

$$S(\text{Tot}) = S(\text{Res}) + S(\text{Int}) = S(\text{Res})/\cos^2 \vartheta = S(\text{Int})/\sin^2 \vartheta. \quad (7)$$

In the cases studied earlier (Curtis 1991) it was found that $S(\text{Tot})$ can be accurately represented by an empirical screening parameter linearization of the form

$$Z^2 S(\text{Tot}) = a + b/(Z - c). \quad (8)$$

Although equations (1)–(7) were obtained from a single configuration picture, the parametric angle ϑ is uniquely defined by equation (3) irrespective of whether or not configuration interaction is present. Its virtue in characterizing these systems is purely utilitarian, judged by the degree of success in producing a linearizing data reduction. If the influence of configuration interaction is indirect in that it alters the singlet-triplet mixing but not the transition integrals, then ϑ will yield a smooth data reduction and the approach will be useful. If configuration interaction affects the transition integrals in ways that are not characterized by the energy level data, then the reduction will not be smooth and the formulation will not be useful.

4. Data sources

This empirical formulation requires an accurate experimental data base of energy levels and transition probabilities. For the Be sequence, energy level data for all four levels of the $2s3p$ configurations are available for Be I (Johansson 1962), B II (Ölme 1971), C III (Bockasten 1955), N IV (Hallin 1966), O V (Bockasten and Johansson 1968), F VI (Engström 1985) and Ne VII (Bockasten *et al* 1963). Differential lifetime measurements for the $J = 1$ and $J = 2, 0$ triplet levels are available for N IV, O V, F VI (Engström *et al* 1979) and Ne VII (Hardis *et al* 1983). For extrapolation purposes, theoretical estimates of the wavelengths and mixing angles (deduced from the ratios $\lambda f(\text{Res})/\lambda f(\text{Int})$) for $14 \leq Z \leq 36$ can be obtained from the *ab initio* calculations of Kim *et al* (1988). For the Mg sequence, energy level data for all four levels of the $3s4p$ configurations are available for Mg I (Risberg 1965), Al II (Kaufman and Hagan 1979), Si III (Toresson 1960), P IV (Zetterberg and Magnusson 1977), and S V and Cl VI (Reistad *et al* 1984). Differential lifetime measurements for the $J = 1$ and $J = 2, 0$ triplet levels are available for S V and Cl VI (Reistad *et al* 1984). For extrapolation purposes,

calculations of the mixing angles for $Z \geq 18$ were made using the multiconfiguration Dirac-Fock code GRASP (Dyall *et al* 1989).

5. Empirical specification of mixing angles

Figure 1 presents plots of $\sin^2 \vartheta$ against Z for the Be 2s3p and Mg 3s4p sequences. The experimental points are denoted by O for the Be sequence and by X for the Mg sequence. Solid lines connect the points and denote the theoretical predictions for higher Z . Both curves exhibit unusual properties caused by configuration interaction.

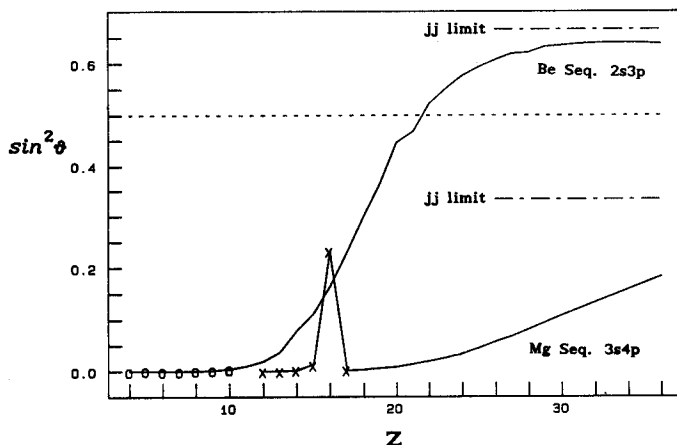


Figure 1. Plot of the singlet-triplet mixing fractions $\sin^2 \vartheta$ against the nuclear charge Z for the 2s3p and 3s4p configurations in the Be and Mg sequence. The experimental points are denoted for the Be sequence by (O) and for the Mg sequence by (X) and solid lines connect the points and denote theoretical predictions for higher Z .

Notice that for the Be sequence, $\sin^2 \vartheta$ approaches a *jj* limit of $\frac{2}{3}$, instead of the value $\frac{1}{3}$ which is normal for a *P*-state. This occurs as the combined result of configuration interaction and an ambiguity in the labelling convention. The \pm sign in equation (3) can be chosen by requiring either $\sin \vartheta \Rightarrow 0$ for small Z or $\sin \vartheta \Rightarrow 1/\sqrt{2I+1}$ for large Z . In most cases these two choices are equivalent, but in this unusual case they are mutually exclusive. Strong configuration interaction effects (primarily with 2p3s) cause a crossing of the $J=1$ eigenvectors between $Z=5$ and 6 and a second crossing occurs at higher Z (between $Z=21$ and 22 as predicted by Kim *et al*) where ϑ passes through 45° . For isoelectronic regularity, it is essential that eigenvectors are treated as crossing where standard labelling conventions would indicate that the energy levels undergo an avoided crossing (cf Maniak and Curtis 1990, Cowan 1981). The 2s3p eigenvector that is followed in figure 1 is the level of lower energy for $Z=4-5$, of higher energy for $Z=6-21$, and of lower energy for $Z>22$. Had the other level been traced, the plot against Z in figure 1 would start at $\sin^2 \vartheta = 1$ and approach the *jj* limit $\sin^2 \vartheta \approx \frac{1}{3}$ from above. It should also be noted that spectroscopic references do not follow the avoided crossing convention at $Z=4-5$, and label the lower energy level as 3P_1 for $Z=4, 5$ (Johansson 1962, Ölme 1970) and as 1P_1 for $Z=6-9$ (Bockasten 1955, Hallin 1966, Bockasten and Johansson 1968, Engström 1985).

The Mg case exhibits a strong peak where $\sin \vartheta$ (plotted as $\sin^2 \vartheta$ in figure 1) jumps from 0.108 at $Z = 15$ to 0.481 at $Z = 16$ and then falls to 0.055 at $Z = 17$. This is a result of a level crossing (or avoided crossing, depending upon convention) with the $3p3d\ ^3P_1$ level, and illustrates the difference between a long range interaction in the same complex (as in the Be case) and an isolated interaction with a plunging level (in the Mg case).

6. Results of line strength reductions

Figure 2 presents a plot of $Z^2S(\text{Tot})$ against $1/(Z-3)$ for the $2s^2$ - $2s3p$ transitions in the Be isoelectronic sequence. Through the use of equation (7), $S(\text{Tot})$ can be computed when either or both of the line strengths $S(\text{Res})$ and $S(\text{Int})$ are available. The experimental measurements for the intercombination transition for $Z = 7, 8, 9$ (Engström *et al* 1979) and 10 (Hardis *et al* 1983) are denoted on the plot by the symbols O, with their uncertainties indicated by error bars. The reduction of these differential lifetime measurements to this line strength assumes complete branching of the intercombination transitions to the ground state. The theoretical calculations of Hibbert (1979) indicate that this branching ratio is 91% for O v, and the calculations of Ellis (1983) show that this branching ratio increases with Z , and is 96% in Ca xvii.

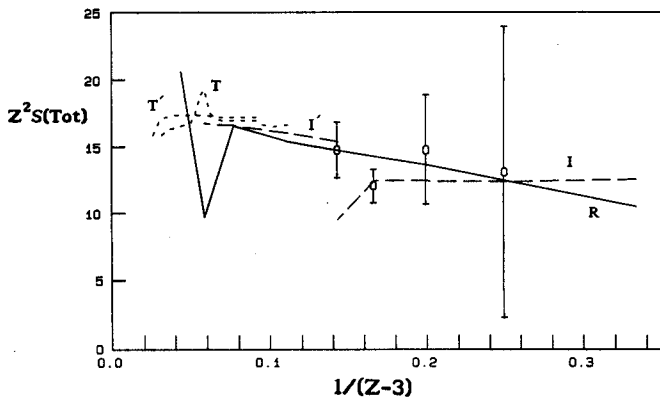


Figure 2. Plot of the charge-scaled total line strength $Z^2S(\text{Tot})$ for the $2s^2$ - $2s3p$ transitions in the Be isoelectronic sequence against the reciprocal screened charge $1/(Z-3)$. Experimental determinations of $Z^2S(\text{Int})/\sin^2 \vartheta$ are denoted by (O), with uncertainties indicated by error bars. The solid line denotes $Z^2S(\text{Res})/\cos^2 \vartheta$ deduced from calculations by (R) Nussbaumer (1972). The dashed lines denote $Z^2S(\text{Int})/\sin^2 \vartheta$ deduced from calculations by (I) Hibbert (1979) and by (I') Ellis (1983). The dotted lines denote $Z^2S(\text{Res}) + Z^2S(\text{Int})$ deduced from calculations by (T) Kim *et al* (1988) and by (T') Sampson *et al* (1981).

In order to investigate the behaviour at higher Z and to complement this exposition of the intercombination line with values for the resonance line, a sampling of theoretical calculations are also plotted in figure 2. Values deduced from the calculations of the resonance transition alone (corrected with $1/\cos^2 \vartheta$) for $6 \leq Z \leq 26$ by Nussbaumer (1972) are denoted by a solid line and the symbol (R). Values deduced from calculations of the intercombination transition alone (corrected with $1/\sin^2 \vartheta$) are denoted by dashed lines with the symbol (I) for work by Hibbert (1979) for $6 \leq Z \leq 10$, and the symbol (I') for work by Ellis (1983) for $10 \leq Z \leq 20$. Values obtained by adding the

theoretical line strengths of the resonance and intercombination transitions are denoted by dotted lines with the symbol (T) for the work of Kim *et al* (1988) for $12 \leq Z \leq 36$, and the symbol (T') for the work of Sampson *et al* (1981) for $12 \leq Z \leq 48$.

Figure 2 demonstrates that this formulation provides an exposition in which all of the experimental and theoretical quantities are slowly varying and nearly linear. The regularity of the measured points is better than their uncertainties would suggest, and weighted least-square fits of a straight line to these data have a slope that is sensitive to the choice of weights. The theoretical calculations plotted here indicate that this mixing angle formulation does indeed permit data for the resonance and intercombination transition probabilities to be combined to specify a single predictive quantity, $S(\text{Tot})$, provided cancellation effects are not severe. However, methods also exist for anticipating cancellation effects, which will be discussed in the next section.

As was described above, for the Mg sequence it is not possible to reduce the available differential lifetime data (Reistad 1984) to a line strength for a single transition because of two factors that have been demonstrated by theoretical calculations (Reistad 1984, Godefroid and Froese Fischer 1985, Brage and Hibbert 1989): (i) the intercombination transitions from the $3s4p\ ^3P_1$ are not dominated by a single channel; (ii) significant J dependence of the experimental lifetimes has been observed only for S v, where a level crossing is expected to introduce substantial J dependence into the triplet-triplet transition probabilities. Despite problems with the direct use of these measurements, the singlet-triplet mixing angle formulation still has applicability to this sequence.

The occurrence of anomalously large singlet-triplet mixing in the $3s4p$ configuration for S v was clearly predicted by the mixing angle data in figure 1. Although the mixing angle obtained from equation (3) is defined through single configuration relationships, the effect of configuration interaction is revealed indirectly as an enhancement of the singlet-triplet mixing. The question that remains is whether the mixing angle obtained from the energy levels specifies the line strengths, or whether configuration interaction also perturbs the dipole transition integral. This can be tested using the calculations of Godefroid and Froese Fischer, who reported calculations for the transition probabilities and wavelengths of the resonance and the intercombination lines of the $3s^2-3s4p$ transition in S v as $A(\text{Res}) = 2.182 \text{ ns}^{-1}$, $\lambda(\text{Res}) = 287.5 \text{ \AA}$, $A(\text{Int}) = 0.4429 \text{ ns}^{-1}$, $\lambda(\text{Int}) = 287.8 \text{ \AA}$. the ratio of these $A\lambda^3$ products yields a value for the mixing angle (neglecting differences in the transition matrices) of $\sin \vartheta = 0.411$, which compares with the value 0.481 obtained from energy level data. This agreement indicates that configuration interaction is here largely accounted for by the mixing angle formulation.

7. Criteria for applicability

The major advantage of this empirical singlet-triplet mixing angle formulation is that it permits the use of measured transition probability data from either the resonance or the intercombination line to be used interchangeably to determine a total effective line strength. This is based on the assumption that the two dipole transition integrals are approximately equal, which will occur only if the exchange splitting of the levels is small and the integrals do not have large cancellation effects. The degree to which these conditions are fulfilled can be examined for specific cases by the use of effective quantum numbers in the context of the Coulomb approximation or quantum defect method.

In the single configuration quantum defect method, cancellations in the transition integral occur as a regular and nearly periodic function of the difference between the effective quantum numbers n_i^* of the upper and lower states. We have developed earlier a simple graphical technique (Curtis and Ellis 1978) for locating regions of large cancellation in an isoelectronic sequence. The method involves plotting the experimentally determined effective quantum numbers for the upper and lower state versus each other, and comparing their positions to the locus of the universally prescribed nodes of cancellation. For physical ions which, when displayed on this plot, exhibit a singlet-triplet splitting that is small compared to the distance to the nearest cancellation node, the two transition integrals should be approximately equal.

Figure 3 presents a plot of n_p^* against n_s^* for the $2s^2$ - $2s3p$ transitions in the Be isoelectronic sequence and the $3s^2$ - $3s4p$ transitions in the Mg isoelectronic sequence. Using the labels assigned in the spectroscopic source literature, the $^1P_1'$ level is denoted by (O) and the $^3P_1'$ level by (X), and the isoelectronic sequences are connected by dotted lines. The solid line denotes a locus of cancellation nodes in the dipole transition integral predicted by the Coulomb approximation (in the functional formulation of Burgess and Seaton 1960). Notice that the plot predicts near cancellations for the resonance transition in Be I, the intercombination transition in Mg I, and for both transitions in Al II. Since the intercombination decay channels have little singlet-triplet mixing for these ions, the effect of their cancellation is not easily detectable, but the cancellations in the resonance transition should be exhibited in anomalously weak (or absent) measured intensities. For the other ions in these sequences, the loci are well separated from the cancellation nodes and the singlet and triplet levels are tightly spaced, so transition integrals of the resonance and intercombination lines should be similar in magnitude.

The approach can also be applied to isoelectronic sequences which possess a substantial singlet-triplet splitting, provided that the points are well separated from all cancellation nodes on this plot. In such cases the regularity of exposition may still

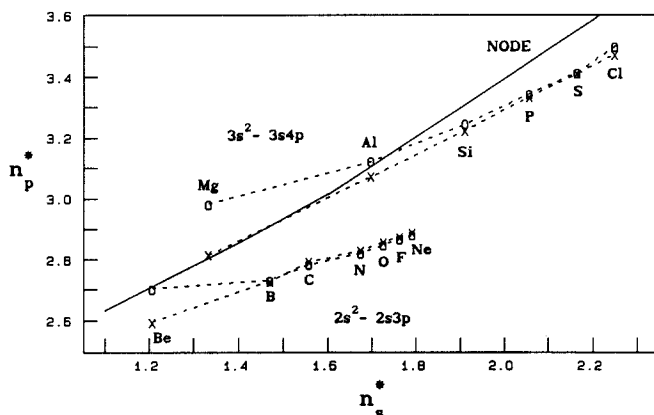


Figure 3. Plot of effective quantum numbers n_p^* against n_s^* for the $2s^2$ - $2s3p$ transitions in the Be isoelectronic sequence and for the $3s^2$ - $3s4p$ transitions in the Mg isoelectronic sequence. The symbols denote: nominal $^1P_1'$ level (O) and nominal $^3P_1'$ level (X). The isoelectronic sequences are connected by dotted lines and the solid line denotes a locus of cancellation nodes in the dipole transition integral predicted by the Coulomb approximation. Note that near cancellations occur for the resonance transition in Be I, the intercombination transition in Mg I, and both transitions in Al II.

be valid, but $S(\text{Res})/\cos^2 \vartheta$ and $S(\text{Int})/\cos^2 \vartheta$ cannot be treated interchangeably. This is the case for the ns^2 - $nsnp$ transitions, which exhibited differing slopes for the resonance and intercombination lines (Curtis 1991).

Previously, this method of studying cancellation effects has been primarily applied to alkali-like sequences, for which intermediate coupling and configuration interaction are not a concern. Thus the cancellations predicted here provide an interesting test of whether the effects of intermediate coupling can be removed by the mixing angle formulation, and whether the effects of configuration interaction can be included through the use of empirical effective quantum numbers in a single channel quantum defect approach.

8. Conclusions

The results presented here indicate that transition probability measurements for extra-shell resonance and intercombination lines in alkaline-earth-like isoelectronic sequences can be systematically combined as complementary empirical quantities. This systematization is achieved through a singlet-triplet mixing angle formulation that utilizes measured spectroscopic energy level data in the empirical reduction of measured transition probability data. The formulation exhibits regularities that permit empirical interpolative and extrapolative predictions, and it can also be applied to theoretically computed results to study the effects of configuration interaction. It provides a method to determine whether configuration interaction has a direct effect on the transition integral, or only an indirect effect through wavelength and intermediate coupling factors.

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